

## PREPARATION OF PERVAPORATION MEMBRANE USING A-TYPE ZEOLITE FILLED CHITOSAN MEMBRANE FOR THE SEPARATION OF ISOPROPANOL/WATER MIXTURES

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**Abstract.** The novel polymeric membranes were prepared by incorporating the NaA zeolite into chitosan and were subjected for the pervaporation separation of water-isopropanol mixtures. The resulting membranes were characterized by Fourier transform infrared spectroscopy (FTIR). The effects of zeolite loading and feed composition on the pervaporation performance of the membranes were analyzed. The membranes were tested for its mechanical properties in terms of tensile strength, elongation and Young's Modulus. The incorporated membrane showed an increase in strength and elongation until it reached its optimum value of 0.3 weight % of zeolite loading in the membrane. The experimental results showed that both flux and selectivity increased with the addition of zeolite content in the membrane. This was explained on the basis of enhancement of hydrophilicity, selective adsorption and molecular sieving action by creation of pores in the membrane matrix.

**Keywords:** Pervaporation; membranes; zeolite; selectivity; incorporated membrane

**Abstrak.** Membran polimer disediakan dengan mencampurkan zeolite A ke dalam larutan chitosan dan akan digunakan untuk pemisahan pervaporasi campuran isopropanol-air. Ciri-ciri membran yang terhasil telah diuji dengan menggunakan Fourier Transform Infrared Spectroscopy (FTIR). Kesan penambahan zeolit dan komposisi suapan ke atas prestasi pemisahan dikaji. Membran juga diuji sifat-sifat mekanikalnya dari segi kekuatan regangan, pemanjangan dan juga Modulus Young. Campuran membran menunjukkan pertambahan dalam kekuatan dan pemanjangan sehingga ia mencapai tahap optimum, iaitu pada 0.3 wt% zeolit dalam membran kitosan. Keputusan eksperimen menunjukkan kedua-dua fluks dan kepemilihan meningkat dengan pertambahan zeolite di dalam membran kitosan. Ini boleh dijelaskan berdasarkan pertambahan sifat hidrofilisiti, penyerapan terpilih dan juga sifat pemilihan molekul oleh pori-pori di dalam susunan matrik membran.

**Kata kunci:** Pervaporasi; membran; zeolit; kepemilihan; campuran membran

### 1.0 INTRODUCTION

Pervaporation is a technique to separate liquid mixtures by means of partial vaporization through a nonporous perm-selective membrane. The permeate will undergo a phase change, from liquid to vapor, during its transport through the barrier.

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Pervaporation is governed by the chemical nature of the macromolecules that comprised the membrane, the physical structure of the membrane, the physicochemical properties of the mixtures to be separated and the permeant-permeant and permeant-membrane interactions [1].

Pervaporation is an alternative method to the conventional method. However, pervaporation performance is depended on the type of membrane used. Chitosan and A-type zeolite are two membrane materials known to have a high hidrophilicity towards water. Eventhough they are hydrophilic in nature, they have different physical and chemical structure, giving them a combine effect when they are incorporated homogenously.

In order to make use of potential available seafood waste in Malaysia, thus the study of chitosan in polymeric membranes is developing and the characterized through pervaporation process, its morphologies and mechanical strength properties have been investigated [2]. However, the performance of pure chitosan membrane is not satisfactory at higher concentration of water due to a large free volume available between the molecular chains [3]. With this, the pervaporation performance can be improved by blending it with other polymers such as polysulfone, PVA, and silk fibroin or by crosslinking it with glutaraldehyde and sulfosuccinic acid (SSA). Alternatively, incorporation of a high selective zeolite into a membrane matrix can also be effective [3].

Zeolites, are crystalline structures that have uniform, molecular sized pores. This organic structure has been used extensively as catalys and adsorbents [4]. Kittur *et al.* [3] have reported that zeolite have a high surface area (up to  $1000 \text{ m}^2/\text{g}$ ), high void volume (30% of the total volume of zeolite) and uniform pore size distribution and hence these have been used widely in chemical and physical processes such as shape-selective catalysis and separation media. In addition, zeolite also has high mechanical strength, good thermal and chemical stability.

In the present work, again an effort has been made to enhance the flux and separation selectivity simultaneously by choosing NaA zeolite and incorporated it into chitosan. The zeolite content with respect to chitosan was varied to improve the membrane performances. The physicochemical changes in the resulting membranes were investigated and the resulting membranes were employed for the pervaporation separation of isopropanol-water. The values of permeation flux and separation selectivity were evaluated. The results were discussed in terms of pervaporation separation efficiency of the membranes.

## 2.0 MATERIALS AND METHODS

### 2.1 Materials

Chitosan powder is supplied by Chitochem company (Malaysia) with the average molecular weight  $MW = 50,000 - 100,000$ . Acetic acid and sodium hydroxide were

supplied from Merck (Germany); ethanol from Fluka (Switzerland) and Isopropanol from J. T Baker (USA). Deionized water from the laboratory was also used in this study.

## 2.2 Membrane Preparation

A pre-weighed chitosan powder was dissolve in 10% aqueous acetic acid solutions for 24 hours at room temperature to produce a casting solution consisting of 1 wt% of chitosan. The polymer solution was filtered to remove the undissolved chitosan and impurities using a vacuum pump. After that, left the solutions overnight at room temperature to release the effervescence and produce a homogeneous solution. The casting solution was pored onto a Petri dish, and leave at a dust free atmosphere for 3-4 days at room temperature. The formed membranes were peeled off from the plate. 3 wt% of NaOH solution containing 47 wt% ethanol and 50 wt% deionised water was used to treat the formed membranes at room temperature for 24 hours. The formed membranes were washed thoroughly with deionised water to completely removed NaOH and dried at room temperature.

Zeolite-filled chitosan membrane was prepared by adding a calculated amount of zeolite NaA (for NaA-filled chitosan membrane) into the solution and mixing thoroughly before casting. The NaA type zeolite will be dispersed well in 10 wt% acetic acid before add in 1 wt% of chitosan powder for 24 hours at room temperature to produce a casting solution. The following procedure was the same with the homogenous chitosan membrane preparation method.

## 2.3 FTIR Experiments

All infrared spectra of the films were obtained with an FTIR spectrometer by using the KBr pellet method and were recorded by an average of 16 scans at a resolution of 4 cm<sup>-1</sup>.

## 2.4 Swelling Tests

The pure chitosan membrane and modified membrane were immersed in 50, 70, 90 and 95% of isopropanol for about 3 days at room temperature. After that, the membranes is dried with a tissue paper and weighed on an analytical balance. The water uptake was calculated according to equation below:

$$DS(\%) = \frac{W_s - W_d}{W_d} (100) \quad (1)$$

where  $W_s$  and  $W_d$  are the mass of the swollen and dry membranes, respectively.

## 2.5 Mechanical Strength Tests

The mechanical strength for both chitosan pure and modified membrane were measured by using Llyord Instrument LRX 2.5KN with cross speed of 5 mm/min. The pure chitosan sample and crosslinked chitosan membrane were being cut into rectangular shape with 30 mm length and 15 mm width. The thicknesses for both membranes were being measured before being tested until they reach their break point.

## 2.6 Pervaporation Experiments

The pervaporation experimental was set up. The selected membrane was tested using 90% feed composition of isopropanol. The feed condition of the process is at room temperature and pressure at atmospheric condition. The modified membrane then compared with the pure chitosan membrane.

The total flux  $J$ , separation factor ( $\alpha$ ) and pervaporation separation index (PSI) are calculated as follows:

$$\alpha = \left( \frac{y}{1-y} \right) \left( \frac{1-x}{x} \right) \quad (2)$$

$$J = \frac{W}{At} \quad (3)$$

$$PSI = J \times (\alpha - 1) \quad (4)$$

Where  $W$  is a mass of permeate (g);  $A$  is a membrane surface area ( $\text{m}^2$ );  $t$  is a time (hr);  $x$  and  $y$  is a weight fraction of the permeate and feed, respectively.

## 3.0 RESULTS AND DISCUSSION

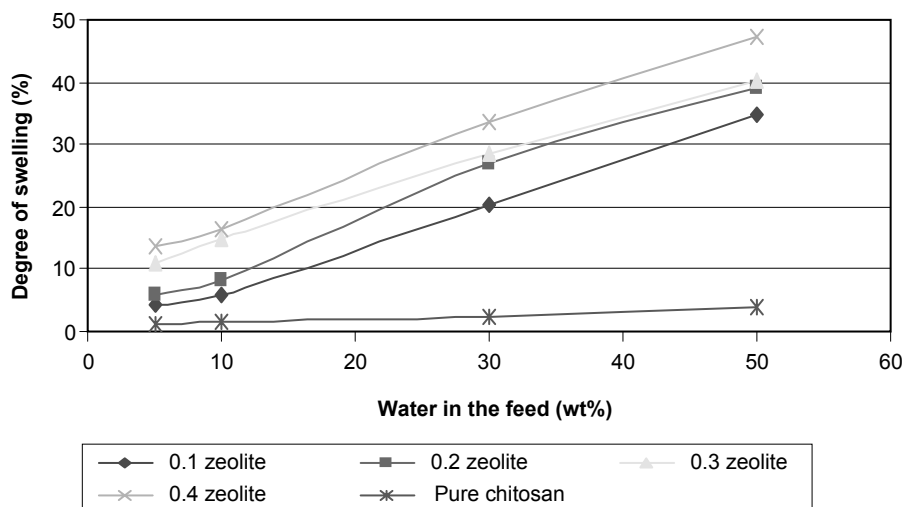
The experiments were carried out in order to study the effect of zeolite loadind in the chitosan membrane to the degree of swelling, mechanical strength and pervaporation of water/isopropanol mixtures. The FTIR analysis was also carried out to prove the characteristic of the unmodified as well as modified membrane. The discussion was made based on comparison of pure chitosan membrane and zeolite-filled chitosan membrane.

### 3.1 Swelling Tests

In pervaporation process, swelling characteristic plays an important role in controlling the transport of the permeating molecules under the chemical potential gradient. Kariduraganavar *et al.* [5] said that, when the polymer matrices are filled with highly

symmetrical zeolite particles, it is likely that the pores of the membranes might be occupied by the zeolite particle.

From Figure 1, it is noted that the degree of swelling increase for all the zeolite incorporated membranes with the increasing weight % of water in the feed. This maybe due to the fact that there is an increase in interaction between water molecules and membrane containing  $\text{-NH}_2$ ,  $\text{-NH}_3^+$ ,  $\text{-OH}$  groups and  $\text{Na}^+$  ions [3].

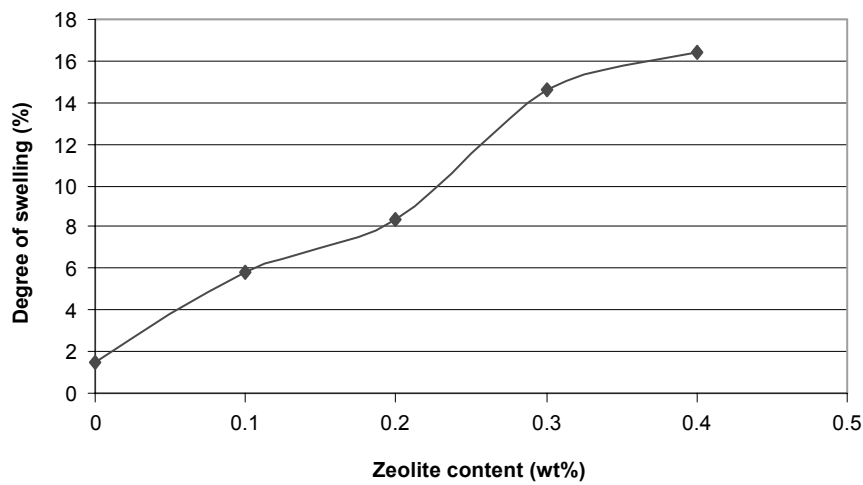


**Figure 1** Variation of degree of swelling with different mass % of water in the feed for different mass % of zeolite incorporated chitosan membranes

Based on Figure 2, when the chitosan are filled with NaA zeolite, the degree of swelling increases more than that of a pure chitosan membrane. This maybe due to the fact that zeolite has a cationic particles, which tends to increase a greater electrostatic force of attraction between water molecules and the membranes [3]. As a result, the adsorption of water molecules increases causing the swelling to increase with the increase of the zeolite content in the membrane.

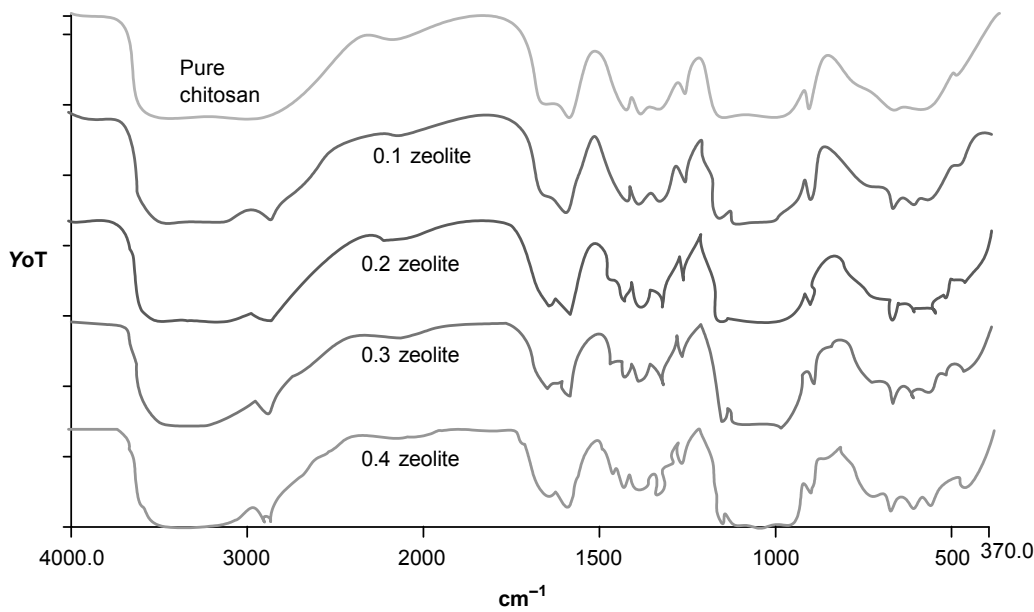
### 3.2 Fourier Transform Infrared (FTIR) Experiments

A Fourier transform infrared spectrometer (FTIR) was used to measure the frequencies of infrared light absorbed that been absorbed by the membranes tested. Based on Figure 3, it can be observed that a characteristic strong and broad band at around  $3440\text{ cm}^{-1}$  in the pure chitosan membrane correspond to O-H stretching vibrations of the hydroxyl group. A strong band appeared around  $1650\text{ cm}^{-1}$  and  $1590\text{ cm}^{-1}$  are assigned to the amino I and amino II functional groups of chitosan, respectively. The intensity of these bands decreased with the addition of zeolite content in the membrane. On the contrary, a multiple peaks appeared between  $1200\text{ cm}^{-1}$  and



**Figure 2** Variation of degree of swelling with different mass % of zeolite incorporated chitosan membranes for 10 mass % water in feed

1000  $\text{cm}^{-1}$  in pure chitosan membrane, are corresponding to the C-O stretching vibrations. The intensity of these peaks did not decrease upon increasing zeolite content in the membranes, this is maybe due to the existance of Si-O groups of zeolite, which appear almost at the same frequency of C-O stretching.



**Figure 3** FTIR spectra of chitosan with addition of zeolite content

### 3.3 Mechanical Strength Experiments

Table 1 shows the tensile strength in Mpa for the chitosan and also zeolite incorporated with chitosan membrane. It is observed that the strength of the membranes decreases drastically from pure chitosan membrane to the addition of zeolite in chitosan membrane. However, it can be observed that 0.3 wt% of zeolite incorporated in chitosan shows an optimum in strength compared to other zeolite filled chitosan membrane. This maybe due to the ideal composition of zeolite that filled in the structure of the chitosan making the links between chitosan molecule and zeolite molecules stronger than the interaction among the chitosan molecules. Therefore, the membrane need higher forces to be broken, which leads to the increase in the tensile strength with the increasing of zeolite content.

**Table 1** The experimental data for mechanical strength test of membranes

<b>Zeolite loading (wt%)</b>	<b>Tensile strength (MPa)</b>	<b>Elongation (%)</b>	<b>Young's modulus <math>\times</math> <math>10^5</math> (MPa)</b>
Pure chitosan	35.21	7.10	2174866.67
0.1 zeolite	16.43	1.70	1223803.33
0.2 zeolite	14.14	1.47	544823.33
0.3 zeolite	22.78	1.96	222170.50
0.4 zeolite	16.87	1.58	562860.00

The same behaviour can be observed with the elongation data, as shown in Table 1. Based on these observations, the membrane exhibits optimum value at 0.3 wt% of zeolite content in the chitosan membrane. From this observation, the elongation of the membrane increase with the addition of zeolite content in the chitosan membrane until it reached its optimum value. This is because the polymer chain of chitosan has the plasticity properties while zeolite has the crystalline structure. The behaviour of the Young's Modulus shows that it decreases until it reached a minimum value which is at 0.3 wt% zeolite and increases afterward until it reached 0.4 wt% zeolite. This behaviour is in contra with the behaviour of the elongation test. Based from the Hooke's Law, with the relation:

$$\sigma = E\epsilon \quad (5)$$

The elongation or strain  $\epsilon$  is inversely proportional with the Young's Modulus ( $E$ ). In general, the chitosan zeolite membrane become stronger toward its optimum value but become more brittle as the zeolite filled membrane is above its optimum value.

### 3.4 Pervaporation Test

Table 2, shows the effect of different composition of zeolite loading on the total permeation flux of the membranes. It is observed that the total permeation flux

**Table 2** The experimental data of water flux, selectivity and pervaporation separation index (PSI) for the pure and modified chitosan

Types of membrane	Total permeation flux ( $\text{g}/\text{m}^2\cdot\text{hr}$ )	Selectivity	Pervaporation separation index, PSI ( $\text{g}/\text{m}^2\cdot\text{hr}$ )
Pure chitosan	7.3	3.245	16.3
0.1 wt% zeolite content	31.6	4.314	136.3

increase from pure chitosan membrane to 0.1 wt% of zeolite content. This is due to the addition of zeolite content that enhances the selective interaction between the water molecules and the membrane. The increasing trend of the NaA zeolite content in the membrane is due to the combination influence of ionic species that exist in the zeolite cages and porous nature of the zeolite and also from the hydrophilic nature of the membrane material [3].

The overall selectivity of a membrane in the pervaporation process is generally determined on the basis of interaction between the membrane and permeating molecules, molecular size of the permeating species and pore diameter of the membrane [5]. It is noted that the selectivity increases with the addition of zeolite content in the membrane. A significant enhancement of hydrophilicity, selective adsorption and molecular sieving action by the creation of pores in the membrane matrix overcome the situation by introducing porous zeolite containing ionic particles in the membrane matrix [3]. The higher water concentration inside the polymer close to the permeate side of the membrane and the fact that the water can travel along a straight path compared to isopropanol, is the reason why the membrane performance is enhanced both in selectivity and flux when zeolite is added to the polymer matrix.

Pervaporation separation index is the product of total permeation and separation factor, which characterizes the membrane separation ability. From Table 2, it is observed that the PSI value increase with the addition of zeolite content in the membrane, showing that the membrane incorporated with zeolite showed better performance for the separation of isopropanol water mixtures. This is because the incorporation of zeolite into a membrane matrix changes not only the membrane's hydrophilicity but also its structure, which may have a significant influence on diffusion [3].

## 4.0 CONCLUSIONS

In general, the preparations of the incorporated membrane were prepared by adding an amount of zeolite NaA into the chitosan membrane that were used to separate the isopropanol-water mixture. The degree of swelling increases for all the zeolite membranes with the increasing weight % of water in the feed. The mechanical test



showed that the unmodified chitosan were stronger compared to the incorporated membrane. The incorporated membranes are said to increase in strength and elongation until it reached its optimum value of 0.3 weight % of zeolite. However, the membrane become more brittle as it reached its optimum value. The FTIR test result all the evidences ascertain the increase of zeolite in the membrane matrix. An increase of zeolite content in the membrane results in the increase of both permeation flux and selectivity. This was explained on the basis of an increase of hydrophilic character, selective adsorption and molecular sieving action by the creation of pores in the polymer matrix. The modified membrane showed increase in pervaporation separation characteristic. Both the flux and selectivity increased resulting in the increasing of pervaporation separation index.

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